On the State of Formic Acid Adsorbed on Dehydrated Silica

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It has been found recently by the kinetic method(1) and by the infrared absorption method(2) in our laboratory that formic acid is chemisorbed as the ion on some metallic powders. However, from the fact that activity of metal as an adsorbent differs from that of silica(3) it is inferred that the acid may be adsorbed on the latter in a different state. To settle the problem some physico-chemical studies were undertaken. A combined method of infrared absorption and proton magnetic resonance was adopted and some conclusions on the chemisorbed state were obtained.

Sample. — The formic acid used in the experiment was dehydrated with anhydrous copper sulfate after repeated distillations. The amorphous silica adsorbent was prepared by dehydrating commercial silica gel at 300°C over a week, and it was confirmed by X-ray analysis that the amorphous structure of silica did not change before and after the dehydration. The specific surface area of silica gel was found to be 520 m^2/g. by the BET method (adsorbate : nitrogen) and formic acid was adsorbed on silica by an amount less than that necessary to form a monolayer*.

Measurement. — The infrared spectra were obtained with the same spectrometer as used in the previous report (Hilger H 800)(2), and a paste method, in which mulling was done with Nujol, was adopted in the present research. The proton resonance spectra were obtained with a high resolution spectrometer (Varian V-4310 C) at a fixed frequency of 40 Mc/sec. Both measurements were made at room temperature.

Results and Discussion.—The infrared spectrum of formic acid adsorbed on silica is quite different from those of formic acid adsorbed on metallic adsorbents which are supported on silica, From the present results shown in Fig. 1, three conclusions may be derived. First, a broad band appears at 3537 cm^{-1}, ranging

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1) K. Hirota and T. Otaki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), in Press.

2) K. Hirota, K. Kuwata and Y. Nakai, This Bulletin, in press (1958).

3) G. M. Schwab et al., *J. Am. Chem. Soc.*, **71**, 1806 (1949).

* The cross section of the formic acid molecule was assumed to be 17 A^2.

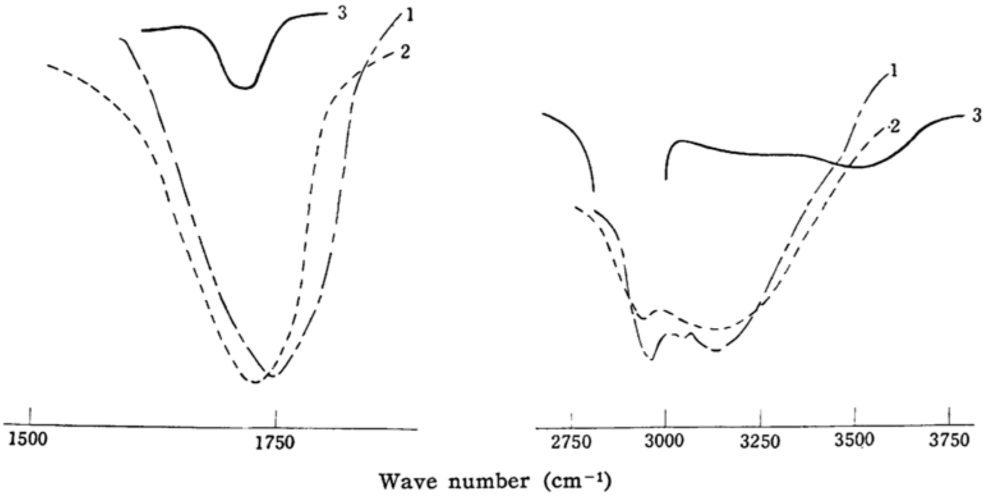
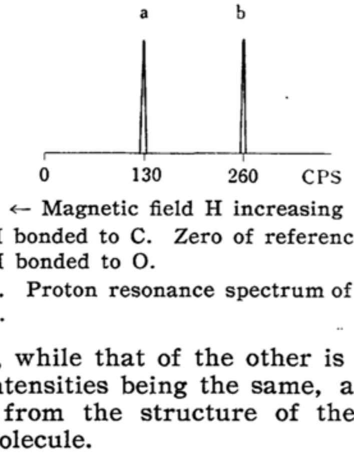


Fig. 1. Infrared spectrum of formic acid in various states.
1: vapour, 2: liquid, 3: adsorbed on silica.

from 3010 to 3765 cm^{-1}*. Such a band did not appear in the cases of formic acid adsorbed on metallic adsorbents and formic acid in the liquid state. According to Bonner and Hofstadter[4] and Wilmshurst[5], associated dimer of formic acid has a broad band near 3080 cm^{-1} which is ascribed to the formation of hydrogen bond, while monomeric formic acid has a sharp band near 3570 cm^{-1}. The band obtained in the present experiment is more similar in frequency to that of monomer than that of associated dimer, but it is broader, probably owing to the interaction between formic acid and silica.

Secondly, the antisymmetric band (ν_4) near 1580 cm^{-1}, which could be assigned to the formate ion $HCOO^-$ in the previous paper[2], is not observed in the present research. This result conforms the above suggestion that formic acid does not dissociate on the silica surface, but exists as a monomeric state. Thirdly, it is found that the C=O stretching band, whose center is at 1717 cm^{-1}, exists in lower frequency than that of monomeric formic acid[5].



← Magnetic field H increasing

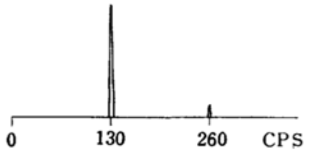
a: ^1H bonded to C. Zero of reference: H_2O
b: ^1H bonded to O.

Fig. 2. Proton resonance spectrum of formic acid.

The above conclusions can also be given by the proton magnetic resonance method, when the spectrum of the adsorbed formic acid is compared with that of liquid. As shown in Fig. 2, the proton resonance spectrum of liquid formic acid gives two proton signals in a lower field relative to that of water. The shift of one signal is 130 cps, while that of the other is 260 cps, both intensities being the same, as is expected from the structure of the formic acid molecule.

It may be assigned from the studies on similar compounds that the former is due to the hydrogen atom bonded to the carbon atom, while the latter to the hydrogen atom bonded to the oxygen atom. To make sure of it, the proton resonance spectrum of deuteroformic acid HCOOD (90% in mol.) was measured. As shown in Fig. 3, the latter signal diminished to one tenth of the former in intensity.

However, the proton resonance spectrum of formic acid adsorbed on silica (Fig. 4)



← H increasing

Fig. 3. Proton resonance spectrum of deuteroformic acid HCOOD (90% in mole).

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* This band is obtained by subtracting absorption intensity of silica alone from that of the system of formic acid-silica.

4) L. G. Bonner and R. Hofstadter, *J. Chem. Phys.*, **6**, 531 (1938).

5) J. K. Wilmshurst, ibid., **25**, 478 (1956).

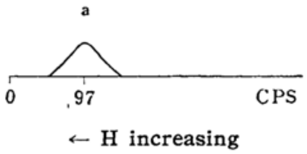

Fig. 4. Proton resonance spectrum of formic acid adsorbed on silica.

is quite different from that in liquid state; i. e., only one signal corresponding to the hydrogen atom bonded to the carbon atom appears as a broad one, its position, moreover, shifting by 33 cps to a higher field. Thus it can be concluded that the motion of hydrogen in the carboxyl group is fixed by adsorption, i. e., its free motion is hindered markedly*. Such a conclusion is in accord with the result that the OH stretching band found in the infrared spectrum becomes broad and shifts to higher frequency. It is supposed that the hydrogen bonds formed in associated formic acid decrease in number as a result of dissociation, caused by the strong adsorption of hydrogen atoms on the silica surface.

It can also be said, from the shift of the signal observed in the proton resonance spectrum of formic acid adsorbed on silica, that the electron density of the hydrogen atom bonded to the carbon atom is increased by adsorption. Detailed discussion on this result will be published later.

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* Recently the proton resonance spectrum of acetic acid, propionic acid etc. adsorbed on amorphous silica was reported (The 11th Annual Meeting of the Chemical Society of Japan, April 6, 1958) by M. Shimizu, T. Ikegami and I. Higuchi. Their conclusion on the adsorbed state is similar to the present one.